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DIFFERENCES IN THE CHARACTER OF C_6 TO C_9 HYDROCARBONS FROM GASEOUS METHANE IN LOW-FREQUENCY ELECTRIC DISCHARGES

By DR. CYRIL PONNAMPERUMA and FRITZ WOELLER

Exobiology Division, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California

IN the study of the chemistry of primitive earth and Jovian atmospheres[1,2], there is considerable interest in the more complex products that may be formed from methane by electric discharges. There is an extensive literature on the reaction kinetics of methane in electric discharges[3,4]. A great amount of work has centred around such factors as power yields, pressure, cell design and presence of hydrogen. Few statements can be found linking these phenomena with possible pathways in primordial chemistry.

In the work recorded here the actions of several arc and semi-corona discharges on gaseous methane were studied. Analysis by gas chromatography and mass spectrometry revealed a significant difference in the type of compounds formed in the two kinds of discharge. An attempt was made to find an explanation for the observed behaviour.

For a source of energy we used a Gardner luminous tube transformer (60 c/s, 120 V input: 15 kV/18 m.amp output; Cat. No. 1518). The two open ends of the secondary were connected to the discharge cell system, and the voltage was regulated by connecting the primary to a Variac autotransformer (General Radio Co. Type *W5LMT3*). Output currents were monitored by a 0–25-m.amp Simpson meter in one branch of the secondary. Voltages were measured with an Electrostatic kilovoltmeter (model *ESD*, Sensitive Research Instrument Corp., New Rochelle, New York). In cases where the 6-kV range would have been exceeded, the voltage was determined as the sum of voltages across three 22 megohm resistors in series. The current through the discharge cell was measured by the voltage drop across a resistor in series with the cell, and this resistor also functioned as a load to limit the current as desired, by using a value between 0·1 and 10 megohms. In two of the experiments described here, we used a pulsed arc which was automatically fired for 3 out of every 30 sec with the help of a Dual-Trol timer (Industrial Timer Corp., Parsippany, New Jersey).

The discharge cell in each case was a 1,000-ml. round flask to which the respective cell heads with their electrode assemblies were attached by wide taper joints.

The semi-corona cell head consisted of a 'Pyrex' tube 100 mm in length, of internal diameter 30 mm with walls 2 mm thick. The inside electrode was made of 6-mm stainless steel tubing extended concentrically throughout the whole length of the 'Pyrex' cylinder. The glass tube was wrapped on the outside with a metal foil which covered 60 mm length in the middle section.

The arc assembly was a short cylinder into which two gold wires, 1 mm in diameter, were inserted. The electrodes were mounted through taper joints. Carbon deposited on the electrodes during the experiment could thus be shaken off by rotating the electrodes. The arc gap was maintained at approximately 10 mm.

The starting material was C.P. methane (99 per cent). At the end of each experiment, we isolated that portion of the cell contents which has more than 1 mm of pressure at $-160°$, and analysed it for the hydrogen–methane ratio using a G.E.C. 21-103 *C* mass spectrometer. After reading the pressure of the remainder, we transferred all those materials which could be distilled and condensed at 40μ mercury and $-78°$ into a capillary cold finger. The volumes of these products were measured by the micro-syringe used to transfer them to an Aerograph *A* 90-*P* gas chromatograph. A 0·25-in. column, 12 ft. long, packed with 10 per cent 'Octoil-*S*' on 60–80 mesh 'Chromosorb-*W*' was used. With helium at 40 ml./min, the absolute retention times were: benzene, 6 min; and toluene, 10 min. This column is similar to 'Apiezon' types, separating hydrocarbons by their boiling points. Fractions collected at $-78°$ were examined in the mass spectrometer.

The data from seven experiments are shown in Table 1. Since the pulsed arc was operated only 10 per cent of the time, the numbers in line 3 give the net hours of current flow. The next line is intended to give a rough guide to the amount of energy consumed in the whole experiment. The apparent electrode voltage and V-amp-h reported for the semi-corona are probably too high, since the voltage has to be divided between the drop across the glass wall and that over the gas space, respectively.

Voltages and currents did not change by more than 30 per cent throughout any of the experiments, and we are listing the averages.

We have tabulated under "% loss of CH_4/h" (Table 1) the percentage of starting material consumed, divided by the number of hours. The volume of distillate reported as microlitres is intended as an illustration of the amount of material actually recovered in each experiment. In all cases the percentage composition of products was independent of the duration of the experiment.

Table 1

	Arc high continuous	Arc high pulsed		Arc low continuous		Semi-corona continuous	
Electrode voltage	2,150	850	1,450	1,275	2,260	8,900	9,425
Cell current (m.amp)	4·5	8	3·5	0·56	0·51	0·4	0·31
Total hours of current flow	5·5	3·8	2·0	21	41	94	41
V-amp-h	53	25·8	10·2	14·5	47·3	335	120
Initial CH_4 (mm Hg)	513	245	504	249	502	255	502
Final press. (mm Hg) CH_4	202	115	385	139	308	39	236
Final press. (mm Hg) H_2	401	177	143	123	192	215	233
Final press. (mm Hg) Others	48	28	19	19	38	8	30
Final press. (mm Hg) Total	651	320	547	281	538	262	499
% loss of CH_4/h	11	14	11·8	2·1	0·9	0·9	1·0
Initial mg CH_4	328	157	323	160	321	163	321
Distillate							
μl.	16	3	2	2	10	4	26
% by vol. C_6H_6	59	53	35	<5	4	<1	0
% by vol. C_7H_8	7	22	24	<5	2	<1	0
% by vol. C_8H_{10}	2	7	7				
% by vol. C_8H_8	7	10	22				
% by vol. others	25	8	12	90	90	95	100
$C_{(s)}$	†	*	*	*	*	—	—
Non-volatiles	†	—	*	*	*	†	*

Note: $C_{(s)}$ and non-volatiles: *, deposit; †, considerable deposit.

In the high-intensity arc the distillate (at 40μ and $-78°$ C) was a clear-yellow fluid which gave chromatograms of well-spaced peaks. On the basis of the peak height, benzene was most abundant. Next in order of magnitude was toluene. A third compound the mass spectrum of which shows a sharp termination at about 106 (C_8H_{10}) corresponds to a boiling point of about 135°, and the fourth suggests a parent mass of about 104 (C_8H_8), and an approximate boiling point of 155°. The mass spectra of both these materials have been obtained, but we have not been able to characterize them using published mass spectral data.

The semi-corona cell yielded a colourless distillate the gas chromatogram of which was poorly resolved. In Fig. 1 this chromatogram (low) has been superimposed on that from the high-intensity arc (high). A significant feature of this trace was the virtual absence of any peaks where benzene and toluene should have appeared. We have obtained a somewhat better resolution at lower column temperature and flow-rate and identified some prominent peaks by mass spectrometry as follows: 2,2-dimethylbutane; 2-methylpentane; 3-methylpentane; 2,4-dimethylhexane; 3,4-dimethylhexane.

The low-intensity arc produced a mixture, the chromatogram of which was similar to that of the semi-corona.

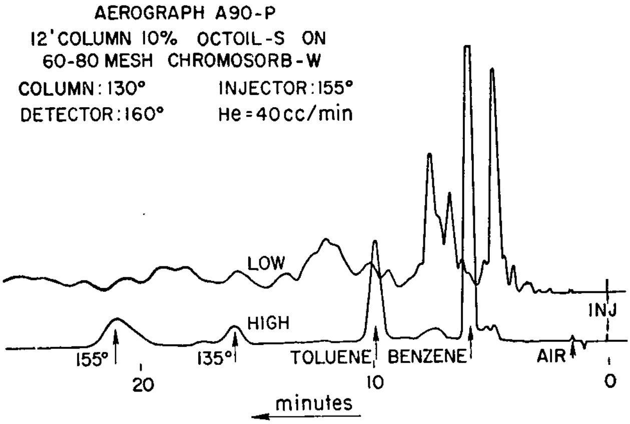

Fig. 1. Gas chromatograms of products from low intensity (semi-corona) and high-intensity (spark-discharge) cells

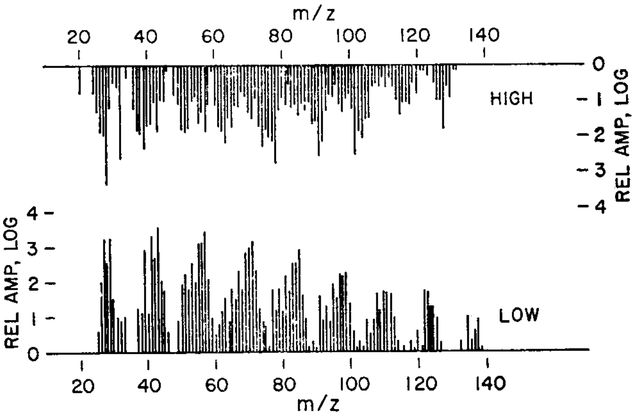

Fig. 2. Portions of composite mass spectra of products from low-intensity (semi-corona) and high-intensity (spark-discharge) cells. The ordinates represent logarithms of relative amplitudes

But, in this case, benzene and toluene were found present in small quantities (Table 1). In Fig. 2, the composite mass spectra of the high arc and of semi-corona products are contrasted to illustrate the differences in the products from the two types of discharge.

The results presented here show that the character of compounds in the range of interest appears to be determined by the type of discharge more than by any other factor. Variations in the duration of the current flow or in the cell dead volume did not at all affect the qualitative results. There is some indication that, at higher initial pressure, the relative yields of C_6 to C_9 material will tend to be higher because these materials have a better chance to condense away from the warm electrode region.

Neither discharge cell showed any gross rise in temperature under air cooling. Further, pulsing the arc brought no departure from the exclusive production of aromatics, while reducing the current did. Metal catalysis due to the gold wires or the stainless steel centre electrode is improbable, because all electrodes were soon covered with carbon deposits. In either case the possible catalytic action of carbon is not excluded.

In an attempt to explain our observations, we may consider that the arc has two primary features which distinguish it from the glow or corona discharge. One is the higher electron temperature, and the other the higher current density of the arc[5]. By inference, ~~we also~~ assume that the local gas temperature in the arc is higher, and that this might result in a depletion of target species in the arc zone. Since a reduction in arc current does not change the current density[6], the results of the low-intensity arc experiments suggest that here the gas temperature is lower than in the case of the high arc. Although there is a tendency toward current localization in the semi-corona after it has been operated for a brief time in this instance, the gas temperature gradient is probably far more moderate.

As it has been suggested that both the spark and the corona-type discharges could have occurred under primitive Earth conditions[7], these findings throw some light on the pathways of formation of aromatic and saturated carbon compounds under abiogenic conditions. In applying our results to the planet Jupiter, it is also conceivable that there is a correlation between the type of hydrocarbon molecule or radical appearing in its atmosphere and the form of the observed energy outbursts[8].

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